Spectrochimica Acta Part A 77 (2010) 6–10

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The vibrational spectra of 1,3-dithiane-1-oxide and 1,3-dithia-1-oxocyclohept-5-ene

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ARTICLE INFO

Article history:
Received 4 December 2009
Received in revised form 19 March 2010
Accepted 22 March 2010

Keywords:
IR spectra
Conformation
Ab initio calculations
1,3-Dithiane-1-oxide
1,3-Dithia-1-oxocyclohept-5-ene

ABSTRACT

The IR spectra of 1,3-dithiane-1-oxide (I) and 1,3-dithia-1-oxocyclohept-5-ene (II) were recorded in solution, solid and liquid phase over 4000–400 cm^{-1} spectral range. It was found that both (I) and (II) in liquid phase and solutions exist in two conformations: (I) chair-e (C_e) and chair-a (C_a) with equatorial and axial positions of the S=O bond, respectively, and (II) chair-e (C_e) and boat-e (B_e). The intensity variations with temperature (300–180 K) of the bands 632 (C_a) and 644 cm^{-1} (C_e) of (I) in acetone-d_6 and the bands 482 (B_e) и 448 cm^{-1} (C_e) of (II) in melt were employed in Van't Hoff plot and gave the values $\Delta H^\circ(C_a - C_e) = 380 \pm 40$ cal mol^{-1} (I) and $\Delta H^\circ(B_e - C_e) = 400 \pm 100$ cal mol^{-1} (II).

Ab initio calculations were carried out with the *Gaussian 98* program using the basis set 6-31G(d) for (I) and 6-311++G(d,p) for (II). The energy difference between C_a and C_e conformations for (I) and B_e and C_e for (II) are in a good agreement with experimental results. Vibrational frequencies for both conformations (I) and (II) were calculated. After appropriate scaling a reasonably good agreement between the experimental and calculated wave numbers was obtained.

1. Introduction

Monosulfoxides of six-membered [1] dithioacetals are now widely used in synthetic practice for the preparation of enantiomerically enriched organic compounds. Many optically active sulfoxides exhibit high biological activity and are important for medicinal and pharmaceutical chemistry [2–4].

The simple representatives of six- and seven-membered dithioacetals 1,3-dithiane-1-oxide (I) and 1,3-dithia-1-oxocyclohept-5-ene (II) are investigated in present work.

Structure and conformational dynamics of (I) have been widely studied by dynamic ^1H [5–9] and ^{13}C NMR [9] spectroscopy. The "frozen" spectra of two conformations in the ratio ~9:1 have been obtained at low temperatures. The dynamic equilibrium of two chair conformations with equatorial and axial position of oxygen ($C_e \rightleftarrows C_a$, Fig. 1) was established. The first conformation appears to be more stable. It is significant that there is an inherent high field shift of C^5 carbon atom of the minor form (I), C_a, [9] relative to dominant conformation C_e (14.7 ppm). *Ab initio*, calculations (I) were carried out in [7], and the energy difference between axial and equatorial conformational was determined (3 kJ mol^{-1}). The similar value was presented in [10]. In [11] *ab initio* calculations at the MP2 (FULL)/6.31G (3df, 2p) level of theory were carried out and the C_e conformation was found to be 7.1 kJ mol^{-1} lower in energy than the C_a form. The experimental energy characteristics of the two-component equilibrium are in a good agreement with the calculated ones [8,9].

Vibrational spectroscopy in combination with *ab initio* calculations allow to receive a valuable information about the structure and conformational mobility of molecules. To our knowledge, the detailed analysis of the vibrational spectra of (I) and (II) is not performed yet.

This work presents new experimental results on conformational dynamics for (I) and (II) based on the IR spectra, *ab initio* calculations and normal-coordinate analysis.

2. Experimental

The infrared spectra were obtained using a Bruker Tenzor-27 spectrometer. The interferograms were recorded with a resolution of 1 cm^{-1}. The number of scans was 32. The sample droplet was squeezed between the KBr plates. Cryogenic investigations were carried out in the standard cryostat. The temperature was registered by means of the platinum thermometer. During all experiments the temperature of the cell was controlled manually,

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doi:10.1016/j.saa.2010.03.035